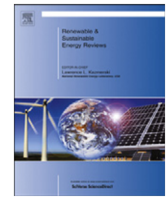
Renewable and Sustainable Energy Reviews 22 (2013) 604–620

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



A review on the evolution of ethyl *tert*-butyl ether (ETBE) and its future prospects

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ARTICLE INFO

Article history:
Received 16 June 2011
Received in revised form
1 February 2013
Accepted 3 February 2013
Available online 17 March 2013

Keywords:
Environmental pollution
Oxygenate additives
Ethyl *tert*-butyl ether
Etherification
Carbon nanotubes
Graphenes

ABSTRACT

The environmental pollution crisis and the new environmental legislations have facilitated the need for cleaner-burning gasoline. Oxygenate additives, which can increase the octane rating and induce complete fuel combustion, play increasingly important roles in the development of a greener and more sustainable environment. In this short review, one of the better-known oxygenate additives, ethyl *tert*-butyl ether (ETBE), is discussed; this compound gained interest after the limitations and negative impacts caused by the addition of methyl *tert*-butyl ether (MTBE) to gasoline were discovered. The discussion focuses on the trends in ETBE production and on the evolution of conventional separation techniques toward the development of hybrid processes. Moreover, a new concept that involves the use of nanomaterials (carbon nanotubes (CNTs) and graphenes) in the production and separation of ETBE is proposed and discussed.

Contents

Abbreviations: A-15, amberlyst-15; A-35, amberlyst-35; ACGHI, American Conference of Governmental Industrial Hygienists; ARCO, Atlantic Richfield Company; [bmin][OTf], 1-butyl-3-methylimidazolium trifluoromethanesulfonate; BRvp, blending Reid vapor pressure; CA, cellulose acetate; CAB, cellulose acetate butyrate; CAP, cellulose acetate propionate; CNTs, carbon nanotubes; CO, carbon monoxide; CSTR, continuous stirred tank reactor; CT-124, CT-145H, CT-151, CT-175, CT-275, ion-exchange resin; DWCNTs, double-walled carbon nanotubes; [emim][$EtSO_4$], 1-ethyl-3-methylimidazolium ethylsulfate; EPA, Environmental Protection Agency; ER, Eley–Rideal; ETBE, ethyl *tert*-butyl ether; EtOH, ethanol; FCSA, flurocarbonsulfonic acid; $H_6P_2W_{18}O_{62}$, Wells-Dawson acid heteropolyacid; $H_6P_2W_{18}O_{62} \cdot 27H_2O$, diphosphooctadecatungstic acid; HC, total hydrocarbon; H-ZSM-5, H-zeolite socony mobil-5; IARC, International Agency of Research on Cancer; IB, isobutene; KU-2–8, gel type ion-exchange resin; LHHW, Langmuir–Hinshelwood–Hougen–Watson; MR, molar ratio; MTBE, methyl *tert*-butyl ether; MWCNTs, multi-walled carbon nanotubes; NO_x, nitrogen oxides; NSTC, National Science and Technology Council; OH^-, Lewis base group; PFR, plug flow reactor; PLA, polylactic acid; PM, particulate matter; PPA, phenylphosphonic acid; PVP, polyvinylpyrrolidone; QH, Quasi-homogeneous; S-115, union carbide zeolite catalyst; $SiO_2 \cdot xH_2O$, silicic acid; $-SO_3H$, sulfonate group; STA, silicotungstic acid; SWCNTs, single-walled carbon nanotubes; *T*, temperature; TBA, *tert*-butyl alcohol; TiO_2, titanium oxide; TPA-K, Keggin-type tungstophosphoric acid; U.S., United States; VA, vinyl acetate; VOC, volatile organic compounds; VP, vinyl pyrrolidone; WHSV, weight hourly space velocity; ZSM-5, zeolite socony mobil-5

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http://dx.doi.org/10.1016/j.rser.2013.02.016

1. Introduction

1.1. History and development of tertiary alkyl ether industry

In the 1970s, the issue of environmental air pollution and the health problems that are caused by automotive vehicle emissions reached a limit that induced great societal concern and the need for strong legislative efforts to reduce automobile emissions [1]. As a result, the exhaust compounds, such as carbon monoxide (CO), nitrogen oxides (NO_x), total hydrocarbon (HC) and particulate matter (PM), were legally regulated. In general, the exhaust compounds can be reduced to an acceptable level in one of three ways: (i) the invention of new engine technologies, (ii) the treatment of the fuel exhaust and (iii) the development and reformulation of existing fuels through the use of additives.

Before the 1970s, gasoline was reformulated through the addition of tetraethyl lead as an antiknock agent to increase the octane rating. However, the utilization of this antiknock agent was terminated when the Clean Air Act of 1970 was enacted. This legislation required drastic reductions in automobile emissions and led to the invention of a catalytic converter by the automobile manufacturers to meet the needs of the legislation. As a result, the vehicles with the catalytic converters required unleaded gasoline to prevent the lead in the tetraethyl lead from poisoning the catalyst system [2]. Methyl *tert*-butyl ether (MTBE) was thus introduced in low concentrations (1–3 vol%) into gasoline as a replacement for tetraethyl lead as an octane booster. In 1979, MTBE was widely used as an octane booster in gasoline component [3].

In 1990, Clean Air Act Amendments were enacted to emphasize the utilization of the oxygenated reformulated gasoline to achieve a better fuel combustion and improve air quality [4]. These amendments set minimum oxygen contents of 2.0 wt% [5] and 2.7 wt% [6] for reformulated gasoline in ozone-nonattainment areas and CO-nonattainment areas in the United States (U.S.), respectively. Moreover, the volatile organic compounds (VOC) emissions can be reduced by setting the blending Reid vapor pressure (bRvp) to a value not higher than 9.0 psi. Thus, these amendments catalyzed the development of MTBE industries, which changed the role of MTBE from an octane booster to a gasoline oxygenate [2].

In 1996, a U.S. Geological Survey study reported that MTBE was frequently found in the urban groundwater supplies sampled [2]. Leakages from the underground storage tanks and pipelines were the primary sources of MTBE contamination. MTBE is quite water soluble and difficult to biodegrade and does not readily adsorb to soil particles; thus, MTBE travels faster and farther than other gasoline constituents if a leakage happens. Moreover, the International Agency of Research on Cancer (IARC) and the U.S. Environmental Protection Agency (EPA) classified MTBE as a health risk threat in 2000 [7]. Although the utilization of MTBE as an oxygenate additive could reduce the amount of pollutants emitted into the atmosphere due to a more complete combustion, its negative effects on water quality have become an issue of debate. A global market report showed that the demand for MTBE increased gradually from 20.6 million tons in 1994 [8] to 21.0 million tons and 22.0 million tons in 1999 and 2002, respectively [2,9]. However, because of the negative impacts that MTBE has on the environment, ETBE has become a popular alternative oxygenate additive for gasoline. ETBE has superior properties compared with MTBE. ETBE was first used in France in 1992. In 2002, France and Spain contributed a total of 568,000 t to the ETBE production capacity in the European Union [10]. The ETBE production capacity increased from 2 million tons to 4 million tons from 2005 to 2007 [9,11]. ETBE is mainly used as a fuel additive in several European countries, including France, Netherlands, Germany, Spain and Belgium [11–13]. Japan tends to produce ETBE using bio-ethanol as one of the reactants [14]. Japanese oil industries started to blend 7% bio-ETBE into automobile fuel in 2010 in accordance with the Kyoto Protocol Achievement Plan [15].

1.2. Fuel additive and oxygenate additive

A fuel additive is a chemical substance that assists the cleaning of engine parts, such as the carburetor, the intake valve and the fuel injector. Fuel additives also play an important role in the reduction of greenhouse gas emissions through complete combustion, the prevention of temper fuel gelling and nozzle choking and the protection of engine parts from corrosion [16]. Fuel additives can be classified into hybrid compound blends, oxygenates (alcohol and ether), antioxidants, antiknock agents, lead scavengers and fuel dyes.

Oxygenate additives contain oxygen as part of their chemical structure and are usually employed as gasoline additives. These additives increment the octane rating and combustion quality and reduce particulate emission and carbon monoxide production [16]. Alcohol and ether are common oxygenate compounds. Alcohols, such as methanol and ethanol, are widely used in automobile fuels. Whereas tertiary alkyl ethers, such as MTBE and ETBE, are commonly used as octane improvers for liquid fuels, their low vapor pressure characteristic reduces the vapor pressure of gasoline [17].

1.3. Advantages and disadvantages of MTBE and ETBE

After the disadvantages of MTBE were revealed, ETBE was found to be an alternative and environmentally friendly octane oxygenate. When the Clean Air Act of 1970 was enacted, MTBE was the most reliable oxygenate additive due to its characteristic behavior. MTBE is non-toxic, has a high octane value and is compatible with the hydrocarbons found in gasoline [2]. However, its impact on health was first revealed after high levels of MTBE were discovered in water wells and groundwater, mainly in North America [1]. MTBE is highly soluble in water (42 mg/L) [9,18] and difficult to biodegrade [9].

Nomenclature

A_f	Arrhenius coefficient for forward reaction, dimensionless
a_i	activity of component *i*, dimensionless
A_r	Arrhenius coefficient for backward reaction, dimensionless
E_a	activation energy, kJ/mol
k_j	reaction rate constants of reaction *j* in the activity-based model, mol/kg·s
K_i	adsorption equilibrium constants, kPa
K_{eq}	equilibrium constant in the activity-based model, dimensionless
K_w	water inhibition parameter in the activity-based model, dimensionless
P_i	Partial pressure of component *i*, kPa
r_j	reaction rate of reaction *j*, mol/kg·s
R	universal gas constant, J/mol·K
x_i	mole fraction of component *i* in liquid mixture, dimensionless
γ_i	activity coefficient of component *i*, dimensionless

According to the U.S. National Science and Technology Council (NSTC), MTBE causes acute symptoms of headaches, nausea, dizziness and breathing difficulties and has an unpleasant taste [19]. The concentration of MTBE should not exceed 30 μg/L to avoid the development of any acute symptoms caused by over-exposures to this compound [1]. At high exposure levels, MTBE has been shown to cause kidney and liver tumors in some rodents [20]. However, at moderate exposures, this compound can cause respiratory inflammation and increase asthma rates [8]. The concentration of formaldehyde, which is toxic, allergenic and carcinogenic, increases with an increase in the MTBE content in gasoline [19]. Moreover, the American Conference of Governmental Industrial Hygienists (ACGIH) (2008) confirmed that MTBE is carcinogen to animal; however, its effects in humans are still unknown [1].

Due to the toxic effect of MTBE on air, water, fuel, engine performance and health, ETBE was chosen as an alternative fuel oxygenate. ETBE has superior qualities as an octane enhancer compared with MTBE; ETBE can be produced from renewable sources, such as bio-ethanol, cellulose, biomass or other farm products [21–24]. Hence, the production of ETBE creates additional markets for grain products and agricultural waste because bio-ethanol, which is used as the raw material in the production of ETBE, can be produced from agricultural feedstock [6,21].

ETBE exhibits a higher octane rating, a higher boiling point, a lower flash point, a lower blending Reid vapor pressure and reasonably high oxygen contents [22–26]. It also has lower volatility and water solubility [1,27] compared with MTBE. Table 1 compares the properties of ETBE and MTBE. Due to the advantageous properties of ETBE, this compound contributes less environmental pollution than any other fuel additive. ETBE reduces the environmental air pollution when it is blended with fuel because it allows complete fuel combustion. Thus, it exhibits a lower emission level of nitrogen oxides and other airborne pollutant, such as formaldehyde and carbon monoxide, compared with MTBE [28]. According to Croezen et al. [29], the substitution of MTBE with ETBE in blended fuel caused a net greenhouse gas reduction of 1.94 kg CO_2/GJ fuel blend.

Moreover, compared with other oxygenate additives, such as ethanol, ETBE does not cause photochemical smog due to its lower blending Reid vapor pressure [14]. Górski et al. [30] revealed that diesel-ETBE blends can reduce particulate matter and smoke emissions by 36% and 70%, respectively. Westphal et al. [1] also found that benzene emissions were significantly reduced by 35% in the exhaust through the addition of ETBE compared with basic fuel without ETBE. The ethyl-benzene, toluene and xylene contents in the exhaust were also reduced. Hence, the addition of ETBE to automobile fuels produces a cleaner-burning fuel that reduces of the emission of environment-polluting gases, increases the fuel oxygen content and enhances the efficiency of combustion.

Table 1
Properties of ETBE and MTBE.

Properties	ETBE	MTBE
Octane rate	112	109
Boiling point	69–70 °C	55.2 °C
Flash point	−19 °C	−10 °C
Blending Reid vapor pressure	27.56 kPa	55 kPa
Oxygen content	15.7 %	18.2 %
Water solubility	23.7 mg/L	42 mg/L

Given the advantages of ETBE compared with MTBE, ETBE has been hailed as the solution for a cleaner and better environmentally friendly fuel additive. However, the production cost of ETBE is generally higher than that of MTBE [31], which would increase the market price of ETBE-blended fuels. However, in Brazil and India, where large quantities of ethanol can be produced, the cost of ethanol, which is used as the raw material for etherification, might become considerable lower than that of methanol, which is derived from natural gas [6,32]. In contrast, the investment cost of ETBE production is considered low because the existing MTBE production plants can be revamped to produce ETBE [33], which is an obviously cheaper alternative compared with building new ETBE production plants. Fernandez et al. [34] reported that the cost of ground water remediation contaminated by MTBE has contributed to the negative cost-benefit analysis of the use of fuels blended with MTBE. The cost of treating ground water contaminated by ETBE can be omitted or expected to be considerably less than that associated with MTBE contamination because the water solubility of ETBE is lower than that of MTBE. Based on the few point of views discussed, the economic feasibility of ETBE as a fuel additive compared with MTBE remains unknown. Therefore, a complete cost-benefit assessment that includes the production cost of both ETBE and MTBE, a market analysis of the demand and supply of both fuel additives, the travel cost, the cost of water remediation and other related costs is required to determine where ETBE has the potential to be used as a future fuel additive for a sustainable and green environment.

2. Production of ethyl *tert*-butyl ether (ETBE)

In general, etherification is an exothermic reversible reaction that converts alcohol to ether. Fig. 1 shows a simplified schematic diagram of ETBE production. ETBE is produced through the reaction of isobutene (IB) or *tert*-butyl alcohol (TBA) with excess ethanol (EtOH). In the industry, the synthesize of ETBE is performed through the use of the liquid phase of IB and ethanol as the reactants and is usually catalyzed by macroporous sulfonic acid resins at a temperature below 80 °C under pressurized conditions of 0.6 MPa [33,35–37]. This synthesis is followed by

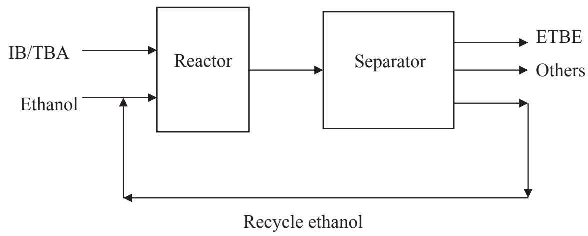


Fig. 1. Schematic diagram of ETBE production.

a series of separation processes to obtain a higher-purity ETBE, and the excess ethanol is recycled to the reactor. The separation techniques are discussed in detail in Section 2.3.

However, the supply of IB is limited because it is obtained from refinery catalytic cracking and steam cracking fractions [18,24,38,39]. In addition, IB is mostly derived from non-renewable crude oil that is also used in other chemical industries, which further reduces the limited supply of this reagent [21]. Hence, there is a need to develop an alternative synthesis for the production of ETBE. Recently, the liquid-phase production of ETBE using ethanol and TBA at atmospheric pressure is gaining increased attention. TBA is a major by-product from the production of propylene oxide in the Atlantic Richfield Company (ARCO) process, which makes it less expensive and thus preferable compared with IB [24,25,39]. There are two ways to produce ETBE from TBA; these can be classified into indirect and direct methods [21,24]. In the indirect method, two steps are used to produce ETBE, as shown in Eqs. 1(a) and 1(b). TBA is dehydrated to IB in the first reaction, and the produced IB is further reacted with ethanol to produce ETBE in the second reaction.

$$\mathrm{TBA} \leftrightarrow \mathrm{IB} + H_2\mathrm{O} \quad 1(a)$$

$$\mathrm{IB} + \mathrm{EtOH} \leftrightarrow \mathrm{ETBE} \quad 1(b)$$

However, in the direct method, only one step is involved, as shown in Eq. (2); TBA is directly reacted with ethanol using an acid catalyst to produce ETBE. Water is formed as a by-product. This direct method is favorable because it involves a single reaction. The catalyst plays an important role in this method to achieve a high activity and selectivity of ETBE.

$$\mathrm{TBA} + \mathrm{EtOH} \leftrightarrow \mathrm{ETBE} + H_2\mathrm{O} \quad (2)$$

2.1. Gas-phase reaction

In the gas-phase production of ETBE, the reactants are in the vapor phase; thus, the partial pressure of the reactants becomes an important variable that affects the formation of ETBE. The gas-phase production of ETBE is less popular than the liquid-phase reaction because it is more difficult and complicated to control the gas-phase reaction. Micek-Ilnicka [40] studied the effect of the feed water vapor on the reaction rate of the production of ETBE via the reaction of IB and ethanol. The reaction was performed in a quartz constant-flow differential microreactor at 40 °C. The partial pressures of IB, ethanol and water vapor were in the ranges of 9–25 kPa, 13–26 kPa and 0.01–8.8 kPa, respectively. The molar ratio of IB to ethanol ranged from 0.4 to 1.5. Wells–Dawson heteropolyacid ($H_6P_2W_{18}O_{62}$) was used to ensure that the conversion was less than 10% such that the effect of the reverse reaction (ETBE decomposition) can be ignored. The results revealed that the addition of water vapor into the feed stream did not change the mechanism of ETBE formation. ETBE could be produced faster by increasing the partial pressure of IB or decreasing the partial pressure of ethanol. However, the presence of water vapor did affect the rate of ETBE formation because TBA was formed as a by-product of the reaction between IB and water. Therefore, increasing the partial pressure of water vapor (the partial pressures of ethanol and IB were maintained constant) accelerates the reaction rate of TBA formation and decreases the ratio of the reaction rate of ETBE to the reaction rate of TBA (r_{ETBE}/r_{TBA}). These results are in good agreement with the findings obtained by Degirmenci et al. [41], who found that the presence of water in the reaction blocked the catalyst active sites and reduced the adsorption of IB and EtOH onto the catalyst surface.

Degirmenci et al. [41] also investigated the effect of the feed composition and temperature on the conversion of IB. The gas-phase reaction was performed in a fixed-bed flow reactor in the presence of heteropolyacid catalysts. The range of temperatures studied was 80 °C to 250 °C, and the IB/EtOH molar ratio was varied between 0.17 and 0.5. Helium was employed as an inert carrier to transport the reactants into the reactor. The results showed that the highest IB conversion to ETBE was obtained at 95 °C and an IB/EtOH molar ratio of 0.17 due to an equilibrium limitation at temperatures above 95 °C. In addition, the penetration of sufficient ethanol into the pseudo-liquid structure of heteropoly acids enhances the sorption of IB into the catalyst structure and leads to a higher IB conversion. In contrast, Degirmenci et al. [42] revealed the inhibitory effect of IB on the dehydration of ethanol to diethyl ether by performing etherifications using EtOH as the sole reactant in the presence of a heteropolyacid catalyst. In the presence of IB, the maximum diethyl ether selectivity was obtained at 200 °C; however, a diethyl ether selectivity of almost 100% was obtained at a lower temperature between 100 °C and 120 °C in the absence of IB as a reactant. The formation of side products, such as diethyl ether, decreased the ETBE selectivity.

Larsen et al. [43] studied the gas-phase reaction of IB and ethanol in a packed-bed flow catalytic reactor at atmospheric pressure. The reaction temperature was maintained in the range of 40 °C to 90 °C. These researchers found that the reaction orders of IB and ethanol were 0.8 and −0.8, respectively, and that the activation energy was 82 kJ/mol in the temperature range of 40 °C to 64 °C. Vlasenko et al. [44] demonstrated that the selectivity of ETBE decreased with temperature in the gas-phase etherification reaction of ethanol and IB conducted in a flow reactor, and catalyzed by sulfonic acid resins. This decrease was due to the natural behavior of a reversible and exothermic reaction, which exhibits the thermodynamic equilibrium limitation at high temperatures. The selectivity of ETBE was found to exceed 80% at a reaction temperature between 80 °C and 100 °C. Moreover, Alcántara et al. [45] studied the influence of the temperature, the molar ratio of ethanol to IB, and the weight hourly space velocity (WHSV) on the yield of ETBE in fixed bed and fluidized bed continuous-flow catalytic reactors. Using IB and ethanol as the reactants, the ETBE yield in the fixed bed reactor was higher than that obtained in the fluidized bed reactor. The highest yield was obtained with a molar ratio of 0.5. The optimum temperatures for the fixed bed and the fluidized bed reactors were 115 °C and 100 °C, respectively. A temperature higher than the optimum temperature tends to shift the reaction toward the reverse reaction because the production of ETBE is an exothermic reversible reaction (enthalpy change, $\Delta H^\circ = -61.83$ kJ/mol). In addition, the maximum WHSVs for the fixed bed and the fluidized bed were 1.5 h^{-1} and less than 0.5 h^{-1}, respectively. Hence, these results show that the use of a fluidized bed reactor in the gas-phase process with zeolite catalysts is restricted due to an attrition phenomenon suffered by the catalyst particles. Large amount of catalysts were removed from the reactor by the gas flow; thus, the catalyst particles had to be recovered and restored to their original size before being reused. Poźniczek et al. [46] studied the effect of the reaction temperature on the yield of ETBE

in the reaction of IB and ethanol. The IB conversion reached its maximum at a temperature in the range of 50 °C to 60 °C. A further increase in the temperature decreased the conversion due to the exothermic behavior of the catalytic reaction.

According to Słomkiewicz et al. [47], the kinetic model for the production of ETBE via the gas-phase etherification reaction of ethanol and IB on sulfonated amberlyst-15 can be expressed as shown in Eq. (3). The measurement of the production rate of ETBE was obtained within the temperature range of 60 °C to 90 °C. The model suggested that, one molecule of ethanol and one molecule of IB are adsorbed during the reaction onto one and two sulfonic groups of the catalyst, respectively. One molecule of ETBE is then desorbed from three sulfonic groups of the catalyst. Langmuir–Hinshelwood equations were used in the calculation of the reaction rate for the production of ETBE at 70 °C. The calculated rate constant was 2.53×10^{-3} mol/min × mequiv SO_3H. In addition, the calculated activation energy was 81.9 kJ/mol. The adsorption equilibrium constants of ethanol (K_{EtOH}) and IB (K_{IB}) of 0.1410 kPa^{-1} and 0.0045 kPa^{-1}, respectively, were required in the calculations.

$$r=\frac{kK_{\mathrm{EtOH}}P_{\mathrm{EtOH}}K_{\mathrm{IB}}P_{\mathrm{IB}}}{(1+\sqrt{K_{\mathrm{IB}}P_{\mathrm{IB}}}+K_{\mathrm{EtOH}}P_{\mathrm{EtOH}})^3} \tag{3}$$

2.2. Liquid-phase reaction

2.2.1. Reaction between isobutene (IB) and ethanol

A significant amount of research is being conducted in the liquid-phase production of ETBE from IB and ethanol [6,35,48]. Similar to the gas-phase reaction, the operating conditions need to be controlled to achieve a satisfactory performance. IB was pressurized to maintain it in a liquid phase for the reaction. The production of ETBE in the liquid phase using IB and ethanol as the reactants over the ion-exchange resin Lewatit K2631 catalyst was reported by Fite et al. [6]. IB was fed from a pressurized cylinder (1.6 MPa) to a continuous-upflow packed-bed microreactor (15 cm length and 4.4 mm inner diameter). Ethanol was stored over 3 Å molecular sieves prior to being fed into the reactor. The molecular sieves dehydrated the ethanol to obtain a water content of less than 0.05% because the presence of water can influence the reaction rates. The reaction temperature and the molar ratio of IB to ethanol were varied from 40 °C to 90 °C and 0.5 to 2, respectively. The results show that the reaction rate is dependent on the molar ratio of IB to ethanol. A faster reaction rate can be achieved by increasing the molar ratio of IB to ethanol: ethanol inhibits the reaction, whereas IB enhances it. Moreover, it was reported that the reaction temperature significantly influenced the reaction rate because the rate decreased by 2.5-fold when the temperature was decreased by 10 °C.

De Menezes and Cataluña [48] investigated and optimized the operating conditions for the production of ETBE. The overall ETBE production scheme consisted of two cylinders that were pressurized to 20 bar and contain a mixture of C_4 hydrocarbons with either 36 mol% IB or 99.5 mol% ethanol. The scheme also consisted of an adiabatic fixed-bed reactor and two distillation columns for the separation of the ETBE/ethanol azeotrope. Amberlyst-15 resin was used to catalyze the reaction. The reaction temperature was varied from 48 °C to 88 °C, and the molar ratio of ethanol to the mixture of hydrocarbons (MR) ranged from 1 to 1.5. Based on the optimization results, the optimum temperature and MR were 62 °C and 1.0 respectively. At the optimum operating conditions, the hydrocarbon conversion was 88%, which resulted in the production of ETBE with the highest degree of purity and minimized the production of ETBE/ethanol azeotropes. In this reversible and exothermic reaction, an increase in the temperature led to a faster reaction rate and a higher conversion. The conversion decreased at temperatures that were higher than the optimum temperature (62 °C), at which the conversion was controlled by the thermodynamic equilibrium. However, a higher temperature is required for higher ethanol feed concentrations to activate the reaction. If the ethanol concentration is increased, the reaction rate decreases because the adsorption of ethanol into the active sites of the catalyst hinders the diffusivity of IB into the catalyst particle. Therefore, the reaction order of the ethanol concentration was negative. This result corresponded to that reported by Micek-Ilnicka [40].

The recent work by Puziy et al. [35] showed the relationship between the reaction temperature and the IB conversion and the ETBE and TBA selectivities. The experiment was conducted in a flow reactor with a fixed bed, and phosphoric acid-activated carbon was used to catalyze the reaction of IB and ethanol. Ethanol was used as an azeotropic mixture that contained 4.43 wt% of water. The reaction temperature ranged from 80 °C to 180 °C, whereas the other process conditions were maintained constant. The study revealed that an increase in the temperature increased the conversion of IB to obtain a maximum value and then decreased the IB conversion due to the thermodynamic limitation. Hence, the highest IB conversion was obtained at approximately 120 °C. The researchers also noted that an increase in the temperature caused a positive increment in ETBE selectivity. The selectivity of ETBE formation increased from 60% to 85% with an increase in the reaction temperature from 80 °C to 160 °C. However, the opposite trend was observed for the selectivity of TBA: a higher reaction temperature caused a decrease in the selectivity of TBA.

Prior et al. [36] estimated this process using batch reactor modelling in the absence or in the presence of insufficient or inappropriate thermodynamic data. Ideal and non-ideal models, which were based on liquid-phase and gas-phase data, respectively, were used for the simulation of the liquid-phase ETBE production from ethanol and IB; an error analysis was conducted to identify the most precise model. The modified Redlich–Kwong equation and the Wong and Sandler mixing rules were used to describe the behavior of the ETBE production, and it was revealed that the non-ideal model results were closer to the experimental data compared with the ideal model results. Moreover, the accuracy of the non-ideal model in the prediction of the evolution of temperature and pressure during the reaction was higher than that obtained with the ideal model; in fact, the error in the non-ideal model was found to be reduced by half of that obtained in the ideal model. Hence, the model generated based on the non-ideal gas-phase data was shown to be more accurate for the study of liquid-phase ETBE production than the ideal model, which was build using liquid-phase data. In addition, the use of residual properties based on the non-ideal gas-phase data might also reduce the dependency on the experimental conditions.

2.2.2. Reaction between tert-butyl alcohol (TBA) and ethanol

Umar et al. [18,25] reacted TBA and ethanol in a five-necked, flat-bottomed, round-top jacketed reaction vessel. The reaction conditions were the following; reaction temperature of 70 °C, molar ratio of ethanol to TBA of 2.0 and agitation speed of 500 rpm. The results revealed that a temperature of 70 °C gave the best conversion and selectivity. The selectivity decreased after 4 h due to the large amount of IB formed in the reaction. A higher molar ratio of ethanol to TBA contributed to the higher selectivity of ETBE. However, a molar ratio of 2.0 was selected as optimum because there was an insignificant difference in the ETBE selectivity within the range of ratios studied. Assabumrungrat et al. [24] reported the production of ETBE from TBA and ethanol in a slurry reactor at 65 °C and 1 atm using β-zeolite supported on

Table 2
Summary of the ETBE production via gas-phase and liquid-phase.

Production of ETBE	Reactants	Important findings	Reference
Gas-phase	Isobutene Ethanol	The addition of water vapor in the feed stream does not change the mechanisms of ETBE formation but it does affect the rate of reaction	[40]
Gas-phase	Isobutene Ethanol	Highest IB conversion to ETBE was obtained at 95 °C and IB/EtOH molar ratio of 0.17. The presence of water in reaction decrease IB conversion	[41]
Gas-phase	Isobutene Ethanol	Inhibiting effect of IB on dehydration of ethanol to diethyl ether	[42]
Gas-phase	Isobutene Ethanol	The reaction orders in IB and ethanol were 0.8 and −0.8, respectively. The activation energy was 82 kJ/mol for temperature range from 40 °C to 64 °C	[43]
Gas-phase	Isobutene Ethanol	Etherification reaction was exhibited thermodynamic equilibrium limitation at high temperature	[44]
Gas-phase	Isobutene Ethanol	The use of fluidized bed reactor in gas phase processes over zeolite catalysts was restricted due to the attrition phenomenon suffered by the catalyst particles	[45]
Gas-phase	Isobutene Ethanol	Maximum reaction temperature was in between 50 °C and 60 °C	[46]
Gas-phase	Isobutene Ethanol	Kinetic study for the production of ETBE from gas phase etherification reaction between ethanol and IB	[47]
Liquid-phase	Isobutene Ethanol	The reaction rate was dependent on the reaction temperature and molar ratio of IB to ethanol	[6]
Liquid-phase	Isobutene Ethanol	The optimum range of reaction temperature and molar ratio of ethanol to the mixture of hydrocarbon were 62 °C and 1.0, respectively	[48]
Liquid-phase	Isobutene Ethanol	TBA was formed as the by-product because of the presence of water in the reaction. The highest IB conversion obtained at temperature about 120 °C	[35]
Liquid-phase	Isobutene Ethanol	The model generated based on the non-ideal gas phase data was showed to be more accurate than the ideal model using liquid phase data	[36]
Liquid-phase	*tert*-butyl alcohol Ethanol	Reaction temperature of 70 °C showed the best conversion and selectivity. The optimum molar ratio of ethanol to TBA of 2.0 was determined	[18,25]
Liquid-phase	*tert*-butyl alcohol Ethanol	Isobutene was produced as the by-product via the dehydration of TBA which mainly in the gas phase. The selectivity of ETBE was high throughout the study	[24]
Liquid-phase	*tert*-butyl alcohol Ethanol	TBA was more rapidly consumed than ethanol and water was more rapidly produced than ETBE. Moderate reaction temperature and high molar ratio of ethanol to TBA could give a high TBA conversion and selectivity of ETBE	[23]
Liquid-phase	*tert*-butyl alcohol Ethanol	Kinetic study for the production of ETBE from liquid phase etherification reaction between ethanol and TBA in the presence of side reaction.	[24,38]
Liquid-phase	*tert*-butyl alcohol Ethanol	Kinetic study for the production of ETBE from liquid phase etherification reaction between ethanol and TBA	[25]

monolith and amberlyst-15 catalysts. The molar ratio of ethanol to TBA was fixed at 1.0. The results showed that IB was produced as a by-product via the dehydration of TBA. The side product (IB) was mainly present in the gas phase. The authors defined the selectivity as the ratio of the amount of ETBE to the amount of water, and the selectivity was found to be high throughout the study.

Yang et al. [23] studied the etherification of ethanol and TBA in the liquid phase under atmospheric pressure for the production of ETBE. Strong acid cation-exchange resins were used as catalysts, and the reaction was conducted in a three-necked, flat-bottomed flask equipped with a condenser. The temperature was manipulated from 50 °C to 65 °C. The molar ratio of ethanol to TBA ranged from 0.5 to 2. Absolute ethanol was not required because water was formed as a by-product in this reaction; thus, this reaction was superior to the reaction of IB and ethanol, in which the purity of the ethanol was crucial because the presence of water would alter the reaction rate. This study showed that the dehydration of TBA produced IB and water and that this reaction was followed by the reaction of IB and ethanol to produce ETBE.

The results revealed that TBA was more rapidly consumed than ethanol and that water was more rapidly produced than ETBE. IB was found in both the liquid and the gas phases. An increase in the temperature increased the TBA conversion but decreased the selectivity of ETBE. At a high temperature, the gas-phase IB increased, which decreased the rate of the reaction shown in Eq. 1(b) and increased the rate of the reaction shown in Eq. 1(a). Therefore, the selectivity of ETBE decreased. In contrast, both the TBA conversion and the selectivity of ETBE increased with an increase in the molar ratio of ethanol to TBA. A moderate reaction temperature and a high molar ratio of ethanol to TBA gave a higher TBA conversion and a higher selectivity of ETBE. Table 2 shows a summary of the gas-phase and liquid-phase ETBE production.

The kinetic model of the production of ETBE from the liquid-phase etherification reaction between ethanol and TBA catalyzed by β-zeolites (Eq. (2)), which takes into account the effect of water inhibition (Eq. 1(a)), was developed and reported by Assabumrungat et al. [24,38]. The rate laws of the reactions were expressed in terms of the activities, as shown in Eqs. (4) and (5). Three temperature levels (50 °C, 60 °C and 70 °C) were used to determine the kinetic parameters in the Arrhenius's equation of the reaction rate constants (Eqs. (6) and (7)) and the van't Hoff's equation of the water inhibition coefficient (Eq. (8)). The expression of k_1 shown in Eq. (9) and the activity coefficients a_i were calculated using Eq. (10). The activity coefficients were calculated using the modified UNIFAC group contribution method [49]. The calculated values of the activation energies of the etherification reaction and the dehydration of TBA were 19 kJ/mol and 114 kJ/mol, respectively. The heat of adsorption of water was 55 kJ/mol. These results indicate that the dehydration of TBA into IB was greatly enhanced with increasing reaction temperature.

$$r_1 = k_1 \frac{a_{TBA} a_{EtOH} - a_{ETBE} a_{H_2O}/K_{eq}}{1 + K_W a_{H_2O}} \quad (4)$$

$$r_2 = k_2 \frac{a_{TBA}}{1 + K_W a_{H_2O}} \quad (5)$$

$$k_1 = \exp\left(3.55 - \frac{2286}{T}\right) \tag{6}$$

$$k_2 = \exp\left(36.57 - \frac{13653}{T}\right) \tag{7}$$

$$K_W = \exp\left(-16.16 + \frac{6636}{T}\right) \tag{8}$$

$$K_{eq} = \exp(1140 - \frac{14580}{T} + 232.9 \ln T + 1.087T - 1.114 \times 10^{-3}T^2 + 5.538 \times 10^{-7}T^3) \tag{9}$$

$$a_i = \gamma_i x_i \tag{10}$$

In contrast, Umar et al. [25] performed kinetic modeling of the liquid-phase production of ETBE using ethanol and TBA and purolite CT-124 as the catalyst. Heterogeneous kinetic models, such as Eley–Rideal (ER) and Langmuir–Hinshelwood–Hougen–Watson (LHHW), were unable to predict the behavior of this etherification reaction. However, a quasi-homogeneous (QH) model was successfully fitted to the experimental data for a wide range of reaction conditions; the reaction rate equations are shown as Eqs. (11) and (12). The expression for the rate constant k_1 for this system was found using the Arrhenius equation, as shown in Eq. (13), and the calculated values of the Arrhenius coefficient (k_1) and the activation energy of ETBE synthesis (E_a) were found to be 1.8×10^5 kJ/mol and 53.455 kJ/mol, respectively.

$$-r_1 = A_f\left(\frac{-E_a}{RT}\right)(a_{TBA}a_{EtOH} - \frac{A_r}{A_f}a_{ETBE}a_{H_2O}) \tag{11}$$

$$-r_1 = k_1\left(a_{TBA}a_{EtOH} - \frac{a_{ETBE}a_{H_2O}}{K_{eq}}\right) \tag{12}$$

$$k_1 = \exp\left(11.827 - \frac{6429.6}{T}\right) \tag{13}$$

2.3. Separation technique

A separation process is required to separate the desire product from the reaction mixtures, which contain unreacted or excess raw materials and the by-products of the reaction. The production of ETBE from ethanol and TBA catalyzed by an acidic catalyst requires a purification process to obtain high-purity ETBE. ETBE, which is the desired product of the reaction, forms azeotropic mixtures with the unreacted ethanol that are difficult to separate by conventional technologies [50–53]. Therefore, a very complex unit operation consisting of four azeotropic distillation columns and one water-washing column are required for the separation process [26,54]. This fact makes the conventional separation methods both expensive and energy-intensive. Most of the difficulties encountered in the separation are due to the azeotropic mixtures that are formed between ethanol, ETBE and hydrocarbons, such as ethanol/hydrocarbon azeotropes, ethanol/ETBE azeotropes and ethanol/water azeotropes [26]. Therefore, combined separation processes or a newly invented separation process would prove useful to obtain a better purification and save energy.

2.3.1. Solvent extraction

In the industrial sector, commercial ETBE is mainly produced in large scale via the reaction of IB and ethanol. Excess ethanol is required for the reaction; thus, ethanol remains after the reaction and is mixed with the product (ETBE). ETBE and ethanol, which have similar boiling points, form an azeotropic mixture with a composition of 78.9 wt% and 21.1 wt%, respectively, at a temperature of 66.9 °C [52]. This azeotropic mixture of ethanol/ETBE needs a series of purification process to obtain high-purity ETBE. This downstream purification stage is typically performed through liquid–liquid separations utilizing an extraction solvent. The addition of the extraction solvent changes the interaction between the components in the azeotropic mixture and hence alters their relative volatilities [55]. Consequently, the azeotropic mixture can be separated.

Water is the most commonly used solvent in the industrial separation of ethers from alcohols because it is inexpensive [48,55]. Recently, ionic liquids and hyperbranched polymers [55] have gained increasing attention in the scientific community as alternatives to water. An ionic liquid is an ionic substance that contains an organic cation with a melting point of less than 100 °C [56]. Hyperbranched polymers are highly branched polydisperse macromolecules with a large number of functional groups. This green solvent has become popular due to its negligible vapor pressure, which implies that it can be fully recovered without contributing to air pollution. Furthermore, this green solvent is able to solvate organic and inorganic compounds and to modify the properties of anions and cations.

Hyperbranched polymers have exhibited good performance in separation processes due to their low melting point, high solubility and remarkable selectivity and capacity [57]. Hyperbranched polymers can also be used as substitutes for organic solvents because these are more environmentally friendly [55]. Domańska et al. [55] investigated the separation potential of two different solvents (ammonium ionic liquid hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate and the hyperbranched polymer Boltorn U3000 (B-U3000)) in the separation of ethanol from ETBE. The results showed that the separation factor was greater than 1 and decreased when the ETBE composition was increased, which restrained the operation to the low ETBE region. This separation factor was approximately 1 if water was used as the solvent. In short, hyperbranched polymers can be a suitable solvent for the liquid–liquid extraction of ETBE from an azeotropic mixture of ETBE with ethanol.

Arce et al. [56] reported the purification of ETBE using the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmin][OTf]) and water as the solvents. The results showed that the solute distribution ratio obtained with [bmin][OTf] was higher than that obtained with water, which implies that this ionic liquid is more effective in the removal of ethanol than water. However, the selectivity obtained when water was used as the solvent was higher than that obtained with [bmin][OTf]. In addition, a higher ethanol concentration in the organic phase decreased the selectivity obtained with [bmin][OTf]. Another reliable ionic liquid that can be used as an extraction solvent is 1-ethyl-3-methylimidazolium ethylsulfate ([emim][$EtSO_4$]). Subsequently, Arce et al. [58] used a simulation approach to study [emim][$EtSO_4$] in the purification of ETBE via an extraction distillation process. The solvent and the feed in equal molarities were fed to a 10-equilibrium-stage distillation column at atmospheric pressure. The top product was pure ETBE and the bottom product was a mixture of ethanol and solvent. The bottom product was heated at 423.1 K before it was fed to a flash vessel (20 kPa). Pure ethanol was obtained from the vessel with 99.1 wt% solvent. The solvent was recycled to the distillation column and reused throughout the process.

2.3.2. Pervaporation with membrane design

The pervaporation technique involves the use of a nonporous selective membrane for the separation of homogeneous liquid mixtures under vacuum conditions (1–3 mmHg) or with the use of an inert sweeping gas in the downstream side of the membrane [50,59]. In pervaporation, the feed is in contact with one side

of the membrane, and the permeate is obtained on the other side of the membrane, which is maintained under vacuum conditions [60]. In general, the minor component, which is usually less than 10 wt%, is preferentially removed from the liquid mixture to achieve good separation. The mass transport in pervaporation involves solution-diffusion mechanisms in which the permeate is dissolved followed by diffusion through the membrane [11]. This diffusion is caused by the strong driving forces that arise from the chemical potential gradient, affinity and diffusivity of the components in the feed mixture toward the membrane.

Many researchers have investigated the performance of different types of membranes for the separation of ethanol and ETBE azeotropes [50,52,53]. The separation of ethanol/ETBE was performed by Roizard et al. [50]. Several routes were investigated to design high-performance membranes for the separation of these azeotropic mixtures. A polymer membrane that exhibits a strong interaction with ethanol was selected for the pervaporation process. Therefore, a polymer with a hydrogen-bond acceptor or a Lewis base group (OH^-) was needed to separate a hydrogen-bond donor (ethanol). Researchers have found that the modification of the polymer structure with a copolymer, such as cellulose acetate (CA), vinyl pyrrolidone (VP) and vinyl acetate (VA), was important to achieve acceptable selectivity and permeation rates for industrial applications. From an industrial point of view, a sustainable composite membrane should continuously release a permeate with at least 95 wt% ethanol from the azeotrope mixture with a minimum flux of 1 $kg/h \cdot m^2$ at 40 °C.

Luo et al. [52] studied the pervaporation process for ETBE and ethanol separation by synthesizing the blending of 30% cellulose acetate butyrate (CAB) with 70% cellulose acetate propionate (CAP). The desired polymer solutions were obtained by separately dissolving CAB and CAP in acetone at room temperature. The solutions were then casted onto PVC plates, and the acetone solvent was evaporated at room temperature for 24 h. The resulted membrane thickness was approximately 50 μm. The results revealed that the permeated ethanol was approximately 98 wt% and that CAP could preferentially interact with ethanol through hydrogen bonding or be dissolved in an ethanol solution at higher temperatures.

Touchal et al. [53] synthesized two types of novel ethanol-selective membranes and investigated their performance in the pervaporation of ethanol and ETBE. The membranes were prepared from pyrrolidinone (NVP) and ionic *N*-substituted methacrylamide (TMA) monomers. The results showed that the pyrrolidinone sites exhibited a strong ethanol membrane affinity due to the Lewis base feature of pyrrolidinone sites towards ethanol molecules. A higher amount of pyrrolidinone residues could enhance the ethanol flux. However, a too-high amount of TMA in the polymer structures could reduce the pervaporation flux because TMA residues act as cross-linking sites and limit the membrane swelling caused by ethanol. In contrast, the results obtained from the blended and copolymer membranes with the same NVP/TMA compositions revealed that the copolymer membrane was more selective to ethanol due to a lower coupling effect.

The performances of blended membranes for the pervaporation of ethanol and ETBE mixtures were reported by Zereshki et al. [11]. The membranes were synthesized by blending polylactic acid (PLA), which is a natural source polymer, with polyvinylpyrrolidone (PVP). PVP is a hygroscopic polymer that has a strong interaction with polar molecules (ethanol). Therefore, it can be used as an additive to control the morphology and hydrophilicity to favor the separation of ethanol from azeotropes through PVP-containing blends. The effect of different PVP loadings and different concentrations of ethanol/ETBE mixtures on the mechanical strength, selectivity and flux were studied. The results show that an increase in the PVP loading led to increased swelling and a higher flux due to the higher ethanol affinity for separation, but a lower Young's modulus. In contrast, increasing the ethanol concentration increases the degree of swelling but decreases the Young's modulus and mechanical strength. The accelerated plasticization effect led to greater sliding of the polymeric chains. Thus, an optimum membrane composition was obtained with an approximately 13 wt% PVP loading based on the maximum separation factor.

The operation variables can also influence the pervaporation flux in addition to the properties and the structure of the membrane. Ortiz et al. [51] investigated the pervaporation of ethanol and ETBE using a commercial membrane (PERVAP 2256). The effective area of PERVAP 2256 was 51.5 cm^2, which consist of a separating layer, a porous polyacrylonitrile support and a non-woven fabric substructure. The pervaporation was conducted as a function of the ethanol feed compositions, which ranged from 30 wt% to 50 wt%, and the temperature, which varied between 50 °C and 70 °C. Both variables exponentially affected the permeate flux. Furthermore, the temperature was found to fit an Arrhenius-type expression. Table 3 shows the different findings that were obtained using different separation techniques.

2.4. Hybrid process

A hybrid process is defined as a process that consists of different unit operations that are interlinked and optimized to achieve a predefined task [61]. The hybrid process can include the combination of a chemical reaction and a separation process or the combination of a series of separation process. The separation process usually involves distillation and/or pervaporation to obtain the desired product purity. For example, the production of ETBE requires a separation process after the reaction to separate the azeotropic mixture of ETBE and ethanol. A high purity of ETBE cannot be achieved through a single conventional distillation column because the boiling points of ethanol and ETBE are very close to each other. Hence, separation units in series, such as pervaporation followed by distillation or vice versa, i.e., the so-called pervaporation–distillation hybrid processes, are required. In general, pervaporation is used to complement distillation when the latter process is inefficient [54]. Pervaporation alone is unable to achieve a high-purity product due to the low mass transfer rate through the membrane. Therefore, pervaporation is usually combined with distillation as a hybrid process to perform the task [61]. In contrast, there are several types of reaction–separation hybrid processes, such as reactive distillation and pervaporation membrane reactors. A hybrid process is an alternative approach to conventional techniques because it offers better energy and cost savings through the utilization of the heat generated during the reaction. A hybrid process also increases productivity by overcoming the chemical equilibrium limitation [61–63].

2.4.1. Pervaporation–distillation hybrid process

A pervaporation–distillation hybrid process offers potential energy savings because it can reduce the thermal energy and pressure required. The recycling of the excess reactants from the hybrid process to the reactor has made this hybrid process more economical through the production of minimal waste and the improvement of the product quality. Hence, a systematic optimization study of hybrid processes should be performed. It is important to evaluate the economical viability, minimize the total cost of the hybrid system, and determine the degree of separation obtained with the pervaporation–distillation hybrid process [64,65]. There are several variables invloved in the optimization, such as the permeate concentration in the retentate stream that is

Table 3
The important findings by using different separation techniques.

Separation	Azeotropic mixture	Important findings	Reference
Conventional distillation	ETBE/Ethanol Ethanol/water	The separation of ETBE/ethanol/hydrocarbon mixtures required four azeotropic distillation columns and one water washing column	[26]
Solvent extraction			
Hyperbranched polymers	ETBE/Ethanol	The overall selectivity was greater than 1 which was higher than water (the solvent used in the industry for separation)	[55]
Ionic liquid	ETBE/Ethanol	The feasibility of the separation process was evaluated by solute distribution ratio and selectivity. The ionic liquid has greater solute distribution ratio than water (more effective in removal of ethanol)	[56]
Ionic liquid	ETBE/Ethanol	Ionic liquid was proven to be the reliable extraction solvent by using simulation approach	[58]
Pervaporation			
Polymer membrane	ETBE/Ethanol	Modifications of the polymer structure with co-polymer was important to achieve an acceptable selectivity and permeation rates for industrial application	[50]
Polymer membrane	ETBE/Ethanol	Cellulose acetate propionate can preferential interact with ethanol through hydrogen bonding or dissolving in ethanol at higher temperature	[52]
Polymer membrane	ETBE/Ethanol	Higher amount of pyrrolidinone residues could enhance the ethanol flux. Copolymer membrane was more selective to ethanol which has limited coupling effect	[53]
Polymer membrane	ETBE/Ethanol	PVP ($\approx$ 13 wt%) could be used as additive onto the polymer blend membrane to achieve the maximum separation factor	[11]
Commercial membrane PERVAP 2256	ETBE/Ethanol	This membrane required longer conditioning time before reaching steady state. Ethanol concentration and temperature showed an exponential trends on the permeate flux	[51]

recycled to the distillation column, which is related to the surface area of the membrane, and the operating conditions of the distillation column (reflux ratio, flow rates of the distillate and intermediate products). Thus, the pervaporation and distillation processes are optimized simultaneously in the context of the hybrid system.

In recent years, pervaporation–distillation hybrid processes have drawn the attention of several researchers; however, the applications of these processes for the production of ETBE are very few. Luo et al. [54] suggested two combinations of distillation and pervaporation schemes for the separation of ETBE-ethanol mixtures. A cellulose-derived membrane was prepared and evaluated using the two separation schemes. In the first scheme, the feed to the distillation column contained 10 wt% ethanol. The azeotropic mixture and ETBE were the top and bottom products, respectively. The azeotropic mixture was further separated with a pervaporator. The permeate was then recycled to the reactor, and the retentate was passed to the distillation column. In the second scheme, the feed containing 30 wt% ethanol was first fed into a pervaporator. The permeate was recycled to the reactor, and the retentate containing 10 wt% ethanol was passed to a distillation column. Then, the azeotropic mixture was passed to the pervaporation unit. Compared with a conventional distillation unit alone, the recovery of ETBE increased from 55.2 wt% to 99.3 wt% using the first scheme. Hence, the integration of a pervaporation–distillation hybrid process plays an important role in upgrading the purity of the product. The schematic diagrams for scheme 1 and scheme 2 are shown in Figs. 2 and 3, respectively.

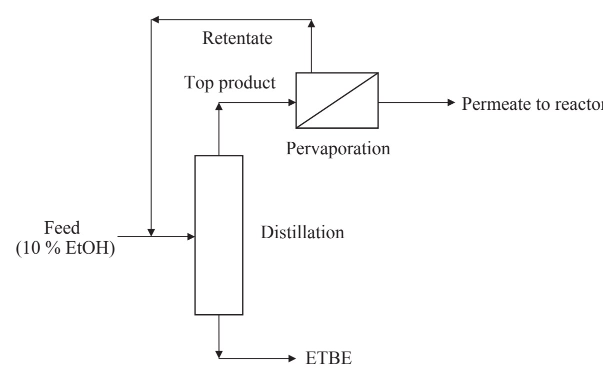


Fig. 2. Schematic diagram of combined distillation and pervaporation (Scheme 1).

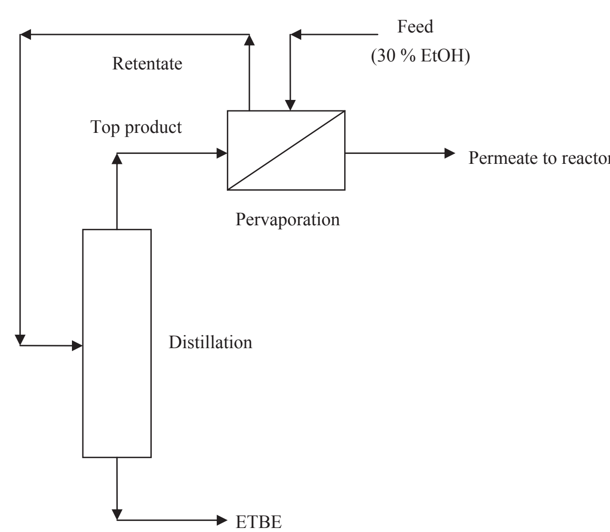


Fig. 3. Schematic diagram of combined distillation and pervaporation (Scheme 2).

2.4.2. Reactive distillation hybrid process

Reactive distillation can be defined as a process in which a catalytic chemical reaction and a separation process occur simultaneously in a single distillation column [66]. This hybrid process is suitable for equilibrium-limited reactions because it shifts the chemical equilibrium toward complete conversion through the continuous separation of the product from the reaction mixture [67]. This hybrid process can significantly reduce the capital and energy costs and eliminates unnecessary downstream processing. The heat released from the exothermic reaction could be utilized for the evaporation of the liquid phase, which could minimize reboiler duty [22]. Therefore, reactive distillation is suitable for the exothermic reversible reaction of ETBE production.

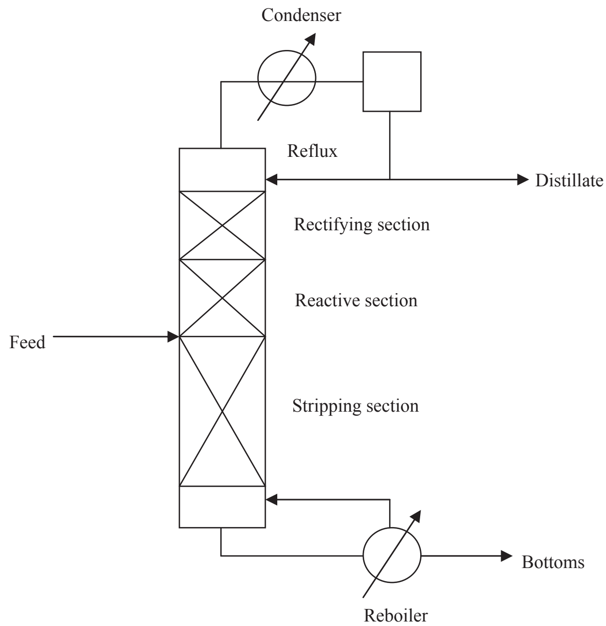


Fig. 4. Schematic diagram of reactive distillation column for ETBE production.

A schematic diagram of a reactive distillation column for ETBE production is shown in Fig. 4.

Assabumrungrat et al. [68] investigated the effects of the condenser temperature, the feed flow rate, the heat duty, the reflux ratio and the molar ratio of water to ethanol in the feed on the performance of a reactive distillation column uisng TBA and ethanol as the reactants. The selectivity of ETBE increased from 27.7% to 43.1% when the condenser temperature was reduced from 60 °C to 30 °C. A lower condenser temperature increases the condensation of ETBE. However, the TBA conversion was not affected by a change in the condenser temperature because the reaction did not occur in the separation zone. Increasing the feed flow rate decreased both the TBA conversion and the ETBE selectivity. However, a reverse trend was observed for the heat duty. The column temperature affected the phases of the reactants, which led to either the forward or the reverse reaction. However, an increase in the reflux ratio had a positive impact on the TBA conversion but decreased the ETBE selectivity. A high reflux ratio was not recommended due to the high energy consumption associated with it. A large amount of water in the feed decreased the TBA conversion and increased the ETBE selectivity. The presence of water altered the concentrations of the reactants and the column temperature, which affected the rate of reaction.

Bisowarno et al. [67] studied the performance of a reactive distillation column for liquid-phase ETBE production from IB and ethanol using acidic ion exchange resins (Amberlyst-15). The design of this column is quite complicated due to the complex interaction between the vapor–liquid equilibrium and the reaction rates. These researchers emphasized the effect of the number of separation and reaction stages on the column performance. The results revealed that the addition of a few separation stages did not reduce the column performance under appropriate operating conditions. However, the use of less separation stages is preferable due to the associated lower energy consumption as long as these exhibit performance that is comparable to that obtained with a column with additional separation stages. Moreover, a column with a longer reactive section could enhance the reaction; however, limited stripping stages might reduce the ETBE purity. A similar performance can be obtained regardless of the number of stages; however, shorter columns are considered to obtain improved energy consumption, operation and control.

The purity of the product obtained through the reactive distillation of ETBE can be maintained by the development of a suitable control scheme. Tian et al. [69] focused on a pattern-based predictive control scheme with controlled reactant conversion and product purity. The control scheme focused on the production of ETBE from IB and ethanol with an acidic ion-exchange resin using pilot-scale reactive distillation. The control

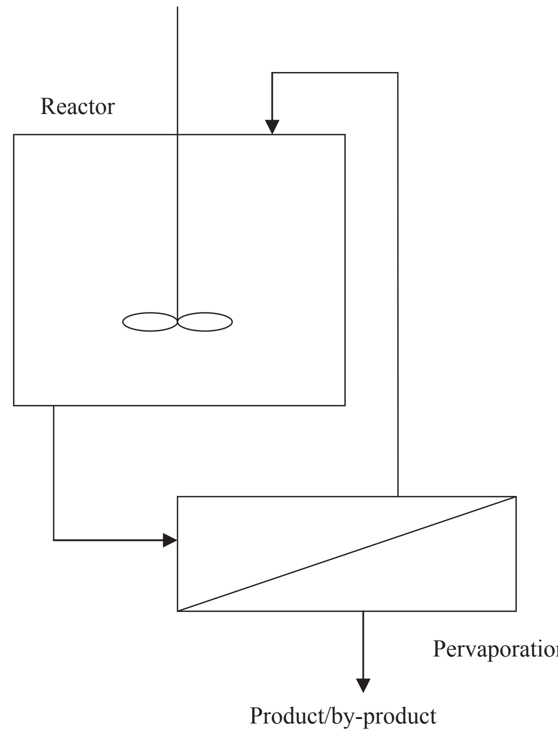


Fig. 5. Schematic diagram of membrane reactor with external pervaporation unit.

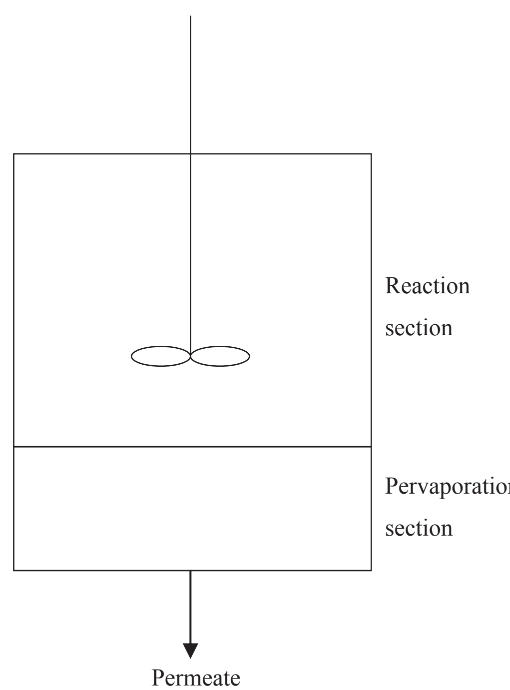


Fig. 6. Schematic diagram of membrane reactor with internal pervaporation unit.

Table 4
Summary of the hybrid processes.

Hybrid process	Azeotropic mixture	Important findings	Reference
Pervaporation–distillation	ETBE/ethanol	Integration of pervaporation–distillation hybrid process plays a significant role in upgrading the purity of the product	[54]
Reactive distillation	ETBE/ethanol	Condenser temperature, feed flow rate, heat duty, reflux ratio and molar ratio of water to ethanol in the feed could affect the performance of the reactive distillation column	[68]
Reactive distillation	ETBE/ethanol	Similar performance can be obtained regardless of the number of stages of the column. However, shorter columns would come into consideration when dealing with the issue of energy consumption, operation and control	[67]
Reactive distillation	ETBE/ethanol	Pattern-based predictive control scheme was revealed to be a promising tool for complex processes and the product purity can be maintained in the reactive distillation of ETBE.	[69]
Reactive distillation with pervaporation	ETBE/ethanol ETBE/water Ethanol/water	The addition of pervaporation placed after reactive distillation was an effective way to enhance ETBE concentration in the top product	[70]
Pervaporation membrane reactor	Not related	Systematic modelling framework was revelaed to be an effective tool to design and analyse pervaporation membrane reactor hybrid process	[71]
Pervaporation membrane reactor	ETBE/water Ethanol/water	Several key variables that should be taken into account in order to achieve high performance of reaction, such as the initial mole of ethanol/TBA, ratio of membrane area/TBA initial mole, ratio of catalyst amount/TBA initial mole, operating temperature and membrane selectivity	[73]
Pervaporation membrane reactor	ETBE/water Ethanol/water	Pervaporation membrane reactor showed superior performance compared to conventioanl reactor with higher selectivity of ETBE and plug flow reactor was preferable to continuous stirred tank reactor	[38]

scheme demonstrated a potential improvement in capital productivity and selectivity. In addition, this scheme can also reduce solvent usage, energy consumption and capital investments. Case studies have shown that this control scheme might improve both set-point tracking and disturbance rejection. Hence, a pattern-based predictive control scheme was revealed to be a promising tool for complex processes.

Yang and Goto [70] proposed the combination of reactive distillation with a pervaporation process to produce ETBE from ethanol and TBA with an ion-exchange catalyst. The additional pervaporation process was placed after the reactive distillation. This hybrid process effectively enhances the ETBE concentration in the top product because the removal of water from the mixture by pervaporation could shift the reaction toward the formation of additional ETBE.

2.4.3. *Pervaporation membrane reactor hybrid process*

A pervaporation membrane reactor combines a chemical reactor and a pervaporation unit, which influence each other during the process; thus, the optimization of this process needs to take into account this interdependency [71]. In general, there are two different designs of pervaporation membrane reactors, which are based on the position of the pervaporation unit, i.e., the pervaporation membrane reactor can have an external or an internal pervaporation unit as shown in Figs. 5 and 6, respectively. Mitkowski et al. [71] investigated a systematic modelling framework to design and analyse a pervaporation membrane reactor hybrid process. Based on the model, it was possible to determine an alternative process design in terms of the process variables, such as the reaction yield, the reaction selectivity and the completion time of the hybrid process. Several steps were required to generate the hybrid model: the collection of reaction data, the determination of the process demands, the selection of an appropriate solvent, the selection of a feasible separation method and the determination of the process conditions. This type of modelling would eliminate the need for unnecessary experiments associated with the optimization of these steps, which would save both time and resources.

The pervaporation membrane reactor hybrid process is an alternative to conventional processes; however, this hybrid process is still in development [72]. Therefore, research on the production of ETBE using these processes is still limited and will likely be explored in the coming years. In the hybrid process, there are several key variables that should be taken into account to achieve a high reaction performance. Kiatkittipong et al. [73] reported that the initial moles of ethanol and TBA, the ratio of membrane area to the initial moles of TBA, the ratio of the catalyst amount to the initial moles of TBA, the operating temperature and the membrane selectivity play important roles on the reactor performance.

The production of ETBE from the liquid-phase reaction of ethanol and TBA in a pervaporation membrane reactor was demonstrated by Assabumrungrat et al. [38]. These researchers investigated the performance of this hybrid process under two different modes of operation: continuous stirred-tank reactor (CSTR) and plug flow reactor (PFR). The operating variables studied were the following: the ratio of the catalyst weight to the total molar flow rate, the ratio of the membrane area to the catalyst weight, the operating temperature and the feed composition. The pervaporation membrane reactor showed superior performance with a higher selectivity of ETBE compared with the conventional reaction alone. The removal of water from the reaction system by the polyvinyl alcohol membrane enhanced the ETBE yield by shifting the equilibrium conversion toward completion. The PFR mode was preferable to the CSTR mode because it achieved a higher yield under mild process conditions. The results also revealed that the operating temperature was the key variable that determined the reaction selectivity. A higher selectivity obtained at a lower operating temperature. A feed ratio of ethanol to TBA that was slightly higher than or equal to the stoichiometric value and a higher ratio of the membrane area to the amount of catalyst increased the yield of ETBE. Table 4 shows a summary of the hybrid processes.

3. ETBE production over different types of catalysts

In the production of ETBE, either via gas- or liquid-phase reaction, the catalyst plays an important role in the acceleration of the reaction toward completion within a short reaction time. Therefore, in addition to the operating conditions discussed previously, the selection of an appropriate type of catalyst becomes one of the factors that can affect the performance of the process. It has been reported that the production of ETBE requires catalysts with Brönsted centres of high acidity [74,75]. In addition, Vlasenko et al. [44] revealed that the production of ETBE was also affected by the mass transfer rate and the adsorption–desorption dynamics

of the reactants and products on the catalysts. The catalysts that had been employed can be grouped into several types: mineral acids, heteropolyacids, acid ion-exchange resins and zeolites catalysts. In 1930s, ETBE was first produced by the reaction of IB and ethanol and the reaction of TBA and ethanol using sulfuric acid as the catalyst [76,77]. Evans and Edlund [77] claimed that sulfuric acid was the best catalyst for ETBE production because it was cheap, exhibited a good reaction rate and the product was easily purified. Norris and Rigby [76] reported that the yield of crude ether obtained using diluted sulfuric acid as the catalyst was higher than that obtained with concentrated sulfuric acid; these yields were 95% and 48%, respectively.

Researchers continue to search for more convenient catalysts due to the negative impact of the sulfuric acid on the environment. Tau and Davis [78] employed different types of acid catalysts to study the impact of the catalysts on the production of ETBE from IB and ethanol. The catalysts used by these researchers were amberlyst-15 (A-15), amberlyst-35 (A-35), zeolite socony mobil-5 (ZSM-5), union carbide zeolite catalyst (S-115), supported fluorocarbon sulfonic acid (FCSA) and phenylphosphonic acid (PPA) resin supported on active carbon. The results revealed that A-15 was an excellent catalyst for ETBE production and slightly better than A-35. Although FCSA resin catalyst had almost the same activity as A-15, FCSA was better than amberlyst because it exhibited a better selectivity for ETBE, was less sensitive to the ethanol/IB ratio, and was thermally stable. FCSA also had a stronger acidity and a longer lifespan [78]. Moreover, the conversion obtained with ZSM-5 was relatively low compared with those obtained with the A-15, A-35 and the FCSA resin catalysts. In addition, S-115 and PPA were inactive for ETBE production.

The commercial production of ETBE through the reaction of IB with ethanol was performed for the first time in 1992 using acid ion-exchange resins as the catalyst [46]. Umar et al. [18,25] performed the etherification reaction using TBA and ethanol as the reactants and ion-exchange resins, which were commercially available, as the catalyst. For comparison purposes, ion-exchange resins, such as purolite CT-124 (gelular matrix), CT-145H, purolite CT-151, CT-175, CT-275, A-15 and A-35, were selected. The researchers found that A-15, A-35 and CT-151 were not suitable from the selectivity point of view. CT-175 and CT-275 showed maximum conversion with low selectivity. CT-124 and CT-145H exhibited similar selectivity. Umar et al. [18] reported that CT-145H was the best ion-exchange resin catalyst because it exhibited a higher conversion than that obtained with CT-124. However, the CT-124 catalyst was better than CT-145H because the ETBE selectivity remained stable for a longer time [25].

Vlasenko et al. [9] synthesized sulfonated poly(styrene-divinylbenzene) ion-exchange resins with different silica gel-supported loadings. The performance of this synthesized catalyst was compared with those of commercial catalysts, such as A-15 and the gel-type ion-exchange resin KU-2-8, in a fixed bed reactor for the liquid-phase reaction of IB and ethanol. The results showed that the acid sites of the loaded sulfonated cation-exchange resin catalyst were more effective for the production of ETBE compared with the commercial catalysts. This results was due to the different location of the acid sites of these catalysts. The acid sites that were located on the surface of the catalyst exhibited better performance than the acid sites located in the depth of the catalyst particles. In addition, a greater acid capacity increased the yield of ETBE.

Although acid ion-exchange resins possess high catalytic activity and selectivity, these also have some disadvantages, such as low mass transfer and thermal stability. Furthermore, ion-exchange sulfonic resins are not stable and evolve sulfuric acid under higher pressures and operating temperatures, which will decrease the catalytic activity and cause environmental damage [75]. Zeolites might be a good alternative to overcome these disadvantages [9]. Assabumrungrat et al. [24] revealed that the ETBE selectivity of β-zeolite was better than that of A-15 (70% and

Table 5
Summary of the catalysts used in the production of ETBE.

Reaction	Catalyst	Important findings	Reference
Isobutene Ethanol	Sulfuric acid	It was claimed that sulfuric acid was the best catalyst for ETBE production	[77]
tert-butyl alcohol Ethanol	Sulfuric acid	The use of diluted sulfuric acid led to high ETBE yield compared to concentrated sulphuric acid	[76]
Isobutene Ethanol	Amberlyst-15 (A-15) Amberlyst-35 (A-35) ZSM-5 Union carbide zeolite catalyst (S-115) Supported flurocarbonsulfonic acid (FCSA) Phenylphosphonic acid (PPA) resin supported on active carbon	FCSA could be a better catalyst for ETBE production among the catalysts studied	[78]
tert-butyl alcohol Ethanol	Different types of acid ion-exchange resins	CT-145H as the most suitable ion-exchange resins catalyst since it showed higher conversion than CT-124	[18]
tert-butyl alcohol Ethanol	Different types of acid ion-exchange resins	CT-124 catalyst was better than CT-145H due to the ETBE selectivity remained stable for a longer time	[25]
Isobutene Ethanol	A new type of ion-exchange resin catalyst; sulfonated poly(styrene-divinylbenzene) resin and commercial A-15	The location of the acid sites of the catalysts could affect the catalytic activity	[9]
tert-butyl alcohol Ethanol	β-zeolite	β-zeolite had shown superior performance over the commercial acid ion-exchange resin	[24]
Isobutene Ethanol	*H*-mordenite catalyst	Zeolite catalysts were thermally stable with no acid effluent and thus suitable to be used to catalyze the reaction	[43]
Isobutene Ethanol	H-ZSM-5 zeolite catalyst	Zeolite catalysts were thermally stable and gave no acid effluent and thus suitable to be used to catalyzed the reaction	[45]
Isobutene Ethanol	Diphosphooctadecatungstic acid, $H_6P_2W_{18}O_{62} \cdot 27H_2O$	Heteropolyacid catalysts were suitable to be used in the production of ETBE	[46]
Isobutene Ethanol	Silicotungstic acid (STA) and Keggin-type tungstophosphoric acid (TPA-K)	High temperature caused the loss of protons and loss of brönsted acidities of heteropolyacid catalysts	[74]
Isobutene Ethanol	Activated carbon supported STA catalyst, cesium salts of STA, activated carbon supported cesium salts of STA and pure STA	20% increased in the conversion of IB to ETBE by using activated carbon supported STA catalyst with 40% STA loading compared to pure STA	[42]

34%, respectively), although the ETBE yields obtained with these two catalysts were almost the same. Hence, β-zeolite showed superior performance over the commercial acid ion-exchange resin and can thus be used as an alternative catalyst for the production of ETBE. In contrast, zeolites catalysts, such as the H-mordenite catalyst and the H-ZSM-5 zeolite catalyst, have been employed in the gas-phase reaction of IB and ethanol at atmospheric pressure [43,45]. Zeolite catalysts were thermally stable without any acid effluent and are thus suitable to be used to catalyze the reaction [78].

Many researchers have studied the characteristics and activities of the heteropolyacid catalysts on the ETBE reaction. Poźniczek et al. [46] studied the production of ETBE by adding ethanol to IB using diphosphooctadecatungstic acid ($H_6P_2W_{18}O_{62}\cdot 27H_2O$) with two different supports (silicic acid ($SiO_2\cdot xH_2O$) and titanium oxide (TiO_2)). The vapor-phase reaction of IB and ethanol was performed using silicotungstic acid (STA) and Keggin-type tungstophosphoric acid (TPA-K), which are the most popular heteropolyacid catalysts [74]. Both types of heteropolyacid catalysts exhibited good performance in the etherification process. However, at temperatures higher than 400 °C, STA lost most of its activity, which led to the loss of protons. TPA-K significantly lost its activity at temperatures higher than 200 °C, and the water of the constitution started to separate from the catalyst at temperatures higher than 500 °C. High temperatures caused the heteropolyacid catalysts to lose protons and Brönsted acidities. In a recent research study conducted by Degirmenci et al. [42], the activities of activated-carbon-supported STA catalysts, caesium salts of STA, activated-carbon-supported caesium salts of STA and pure STA in gas-phase etherification were compared. The results showed that a 20% higher conversion of ETBE was obtained using activated-carbon-supported STA with a 40% STA loading compared with pure STA due to the increased surface area obtained after the impregnation of STA onto an activated-carbon support. However, the activity of activated-carbon-supported caesium salts of STA was lower than the activity of activated-carbon-supported STA due to the lower acidity of the caesium salts of STA compared with STA. Table 5 shows a summary of the catalysts used in the production of ETBE.

4. Limitation of conventional methods in the production of ETBE

ETBE has been the most reliable alternative for MTBE after it was found the MTBE contributes to the pollution of ground water. Conventionally, ETBE was produced from IB and ethanol using acid-based catalysts. However, IB suffers from the limited supply obtained from refinery catalytic cracking and steam cracking fractions. The operating pressure needs to be maintained above atmospheric pressure to pressurize IB, which would increase the energy consumption. Therefore, a more promising liquid reactant should be selected. TBA, which is the major by-product of the production of propylene oxide in the ARCO process, can be employed. The production of ETBE from TBA and ethanol does not require a high operation pressure; in fact, it can be performed at atmospheric pressure. The utilization of TBA as the reactant for ETBE production should be given greater consideration because it allows a safer operating environment and is more reliable from a sustainability point of view compared with IB.

The limitation of conventional distillation for the separation of azeotropic mixtures has urged researchers to search for alternative separation methods. A series of separation units do not appear to be an economically beneficial solution because the operating and capital costs would be increased. The problem can be solved through the combination of a distillation column with a pervaporation unit. Hybrid processes have recently become an attractive technique for the combination of a chemical reaction with a separation process in a single step. As discussed previously, reactive distillation and pervaporation membrane reactors have gained huge interest from researchers for the production of ETBE in either the gas- or the liquid-phase. Moreover, a pervaporation membrane reactor is superior to reactive distillation for the production of ETBE. This result is due to the continuous separation of water (by-product) from the reaction mixture by pervaporation which favors the forward reaction and thus decreases the reaction time. Yang and Goto [70] used two types of membranes within the same reactor in combination with reactive distillation: one of the membranes was used to remove water and the other was used to remove ETBE by pervaporation.

In the previous discussion, it was shown that several catalysts can be employed in the production of ETBE. Catalysts with strong acidic properties would more favorably catalyze the reaction. Acidic ion-exchange resins are conventional catalysts that have been commercially employed. However, researchers are still searching for advanced catalysts to achieve a more economical and environmentally friendly process. In this paper, carbon nanotubes (CNTs) and graphene were analyzed as catalyst support for the production of ETBE from TBA and ethanol in a pervaporation membrane reactor.

5. Recommendations

5.1. Carbon nanotubes (CNTs)

CNTs are seamless cylinder-shaped macromolecules with a radius as small as a few nanometers and a length of up to several micrometers [79,80]. The walls of theses tubes are constructed of a hexagonal lattice of carbon atoms, and the tubes are capped by fullerene-like structures. There are two types of carbon nanotubes: multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). MWCNTs are composed of two or more concentric cylindrical shells of graphene sheets that are coaxially arranged around a central hollow area with spacing between the layers [79]. In contrast, SWCNTs consist of a single concentric cylindrical shell of graphene sheet; the length of SWCNTs is a million times longer than their diameter [81]. In addition to MWCNTs and SWCNTs, there is another special type of carbon materials: double-walled carbon nanotubes (DWCNTs). DWCNTs have coaxial structures that are produced by heating or electron irradiation such that the fullerenes are decomposed into a single inner CNT shell. DWCNTs occupy a position between MWCNTs and SWCNTs [82,83]. CNTs exhibit advantages among carbon materials due to their physical, thermal and electrical properties. It has become clear that the mechanical properties of CNTs are better than those of any existing materials [84]. The Young's modulus is as high as 1.2 TPa, and the tensile strength of these materials is 50–200 GPa [85]. Therefore, CNTs have a wide range of potential applications in the field of semiconductors, super-capacitors, waste water treatment, air pollution monitoring, biotechnology, renewable energy, energy storage and catalyst supports [84,86]. Table 6 summarizes the physical properties of CNTs.

Table 6
Physical properties of different carbon materials [115–117].

Property	Unit	SWCNTs	MWCNTs
Specific gravity	g/cm^3	0.8	1.8
Electrical conductivity	S/cm	10^2–10^6	10^3–10^5
Electron mobility	$cm^2/(Vs)$	$\approx 10^5$	10^4–10^5
Thermal conductivity	W/(mK)	6000	2000
Thermal stability in air	°C	>600	>600
Specific surface area	m^2/g	$\approx$ 400–900	$\approx$ 200–400

CNTs are synthesized into sheets or films known as buckypapers for various types of applications. These buckypapers have been investigated to determine their potential use as super-capacitors, electrodes, gas separators, field emitters, actuators, sensors, artificial muscles and hydrogen storage materials [87–92]. In general, buckypapers consist of a tangled network of CNT ropes and bundles and some individual tubes that are held together by non-covalent interactions [92]. These buckypapers have been fabricated using SWCNTs [88,90,92–95], DWCNTs [96] and MWCNTs [89,91,97–99] via sonication [88] or electrophoretic deposition (EPD) [97] techniques. CNT buckypapers have good properties, such as a high specific surface area, high porosity and high handleability [96,100,101].

This review paper proposes the use of MWCNTs buckypapers as the selective membrane in separation processes. Another more advanced potential application of CNT buckypapers is their use as catalytic membranes. In this application, the functionalization of CNT buckypapers is required to introduce the functional groups onto the sidewall of the CNTs. These functional groups behave as catalysts in the reaction. For the etherification reaction used to produce ETBE, the sulfonate group ($-SO_3H$) can be functionalized onto the CNTs before these are synthesized into buckypapers. Without functionalization, most of the CNTs suffer from a lack of binding sites and exhibit poor dispersion, which causes the CNTs to agglomerate, especially at a high CNT loading, due to the strong van der Waals forces between them [102]. Hence, functionalized CNT buckypapers play an important role in the catalysis of chemical reactions and the separation of the desired components in a pervaporation catalytic membrane reactor. However, self-supporting CNT buckypapers might exhibit a low tensile strength and structure. The properties of CNT buckypapers can be enhanced through the incorporation of polymer composites [88,90,93,94]. CNT-polymer-composite buckypapers have many advantages compared with self-supporting CNT buckypapers: a better uniform dispersion and a controlled structure of the nanotubes [103].

5.2. Graphene

Graphene has become an interesting topic of discussion in recent years. There are still many aspects that need to be explored and investigated, including the structure and properties of graphene, which are controlled by the synthesize methods. In general, graphene is the mother of all graphitic forms, including zero-dimensional fullerenes and one-dimensional and three-dimensional graphite [104,105]. It is the thinnest known material in the universe with a two-dimensional one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed into a honeycomb crystal lattice [106–108]. Graphene was initially obtained by the mechanical cleavage of graphite; however, this method has a very low productivity, which makes it unsuitable for large-scale production. Chemical conversion from graphite provides stable suspension sheets of graphite oxide in water, which can be subsequently reduced to graphene at a low cost [109]. However, a suitable method for the large-scale production of graphene is still under investigation [110].

There are three different structures of graphene, which are determined by the layer quantity: single-layer (one layer of a two-dimensional hexagonal sheet), bi-layer (two layers of a two-dimensional hexagonal sheet) and few-layer (three-to-ten layers of a two-dimensional hexagonal sheet) graphene [111]. Choi et al. [107] reported that single-layer graphene is one of the strongest materials with a predicted Young's modulus of approximately 1.0 TPa, a unique electronic structure, gas sensing ability and ambipolar characteristics at room temperature. Bi-layer and few-layer graphene are considered gapless semiconductors, although few-layer graphene provides a higher surface area and better gas adsorption properties and is more easily functionalized through either covalent or non-covalent modifications. In short, graphene exhibits excellent properties, including high thermal conductivity, great mechanical strength, which is comparable to that of CNTs, superior transport properties and great thermoelectric effect [112]. The unique characteristics of graphene have made it suitable for a wide range of applications. Potential graphene applications include high-speed and radio-frequency logic devices, thermally and electrically conductive reinforced composites, batteries, practical sensors, field effect transistors and transparent electrodes for displays and solar cells [105,107]. The reported potential applications of graphene are in the technological fields of nanoelectronics, supercapacitors, batteries, sensors, hydrogen storage and nanocomposites. However, there are still no reports regarding the utilization of graphene through the form of graphene papers in a pervaporation catalytic membrane reactor for ETBE production.

The synthesis of graphene papers involves a few procedures. These include the vacuum filtration of graphene dispersions through a membrane filter followed by air drying. Subsequently, the graphene papers are peeled from the filter and annealed at temperature [113]. Few-layer graphene might be the best candidate among the graphenes for the fabrication of graphene papers due to its structure and characteristics. Graphene papers, which have a high surface area and high thermal stability, exhibit excellent water-resistance behavior: these cannot be re-dispersed into water by ultrafiltration [109]. Moreover, the Young's modulus and tensile strength of graphene papers are 41.8 GPa and 293.3 MPa, respectively, with a 220 °C annealing temperature [113]. However, highly hydrophobic graphene sheets with strong van der Waals interactions can easily agglomerate [112]. This agglomeration can be reduced through the functionalization of the graphene papers with other molecules or polymers [109]. This functionalization can achieve stable dispersions of graphene and optimize the microstructure of the nanocomposites [112]. In addition, the functionalization of graphene sheets is important for its application in the catalytic chemical reaction for the production of ETBE. It is necessary to graft $-SO_3H$ onto the graphene surfaces through functionalization such that this functional group can act as the active site for the catalytic reaction. The charged $-SO_3^-$ units can also prevent the aggregation of the graphitic sheets [114]. Therefore, the functionalization of graphene should be performed before the graphenes are synthesized into graphene papers.

Based on the above discussions, it is evident that functionalized CNT buckypapers and functionalized graphene papers might be suitable for use in a pervaporation catalytic membrane reactor because these buckypapers can catalyze the chemical reaction and serve as a separation barrier in the pervaporation process. Hence, a hybrid process that involves a chemical reaction and separation processes that occur simultaneously within the same apparatus might be an interesting, energy-saving and environmentally friendly process in the coming future.

6. Conclusions and future outlook

An effort to overcome environmental pollutions, such as air and water pollution, has been stimulated after the Clean Air Act, which mandated drastic reductions in automotive vehicle emissions, was enacted in 1970. In response to this legislation, there was a great evolution in the automotive industries that required the replacement of leaded gasoline with unleaded gasoline through the use of MTBE as an octane booster in gasoline. The enacting of the Clean Air Act Amendments of 1990 urged a change in the role of MTBE from octane booster to gasoline oxygenate. However, a debate on the safety of and the health issues caused by MTBE began in the U.S. after it was discovered that MTBE contributed to underground water pollution.

The use of ETBE as an oxygenate additive is an alternative to MTBE for the reduction of air pollution without causing negative impacts on human health. ETBE has promising properties and characteristics, such as a lower volatility and water solubility, compared with MTBE, which helps minimize its effect on environmental pollution through the emission of a lower level of nitrogen oxides and other airborne pollutants, such as formaldehyde and carbon monoxide. Moreover, ETBE, which can be produced from renewable sources, such as bio-ethanol, cellulose, biomass and other farm products, has superior qualities as an octane enhancer compared with MTBE.

In general, ETBE can be produced by reacting IB with ethanol or reacting TBA with ethanol. The etherification reaction between IB and ethanol could occur either under pressurized conditions (liquid-phase etherification) or under atmospheric pressure (gas-phase etherification). However, most researchers prefer to use a liquid-phase reaction because it is easier to control the process variables. Therefore, more emphasis has been placed in the production of ETBE from TBA and ethanol because TBA has a higher boiling point (82 °C) than IB (−6.9 °C), which makes it possible for the reaction to occur under atmospheric pressure. Furthermore, TBA is relatively less expensive because it is a major by-product of the ARCO process. Several experimental works have confirmed that the presence of water vapor in the feed is not favorable for the etherification reaction of IB and ethanol. Thus, absolute ethanol is required because water affects the rate of reaction and induces the occurrence of a side reaction, which reduces the selectivity and yield. However, absolute ethanol is not required for the etherification reaction with TBA because water is formed as by-product in the reaction. It is also interesting to note that the optimum operating temperature of the TBA etherification (70 °C) is lower than that of the IB etherification under pressurizes conditions (120 °C).

The catalyst plays an important role in the etherification reaction because it accelerates the reaction toward completion. Different types of catalysts, such as mineral acids, heteropoly acids, zeolites and ion-exchange resins, have been studied. The properties of the catalysts and, more specifically, the location of the acid sites of the acidic catalysts are important factors that contribute to the catalytic activity. Initially, researchers claimed that sulfuric acid was the best catalyst for ETBE production. Then, ion-exchange resins and zeolites catalysts were employed in the etherification reaction because it was found that sulfuric acid is harmful to the environment. In the last decade, researchers have revealed that zeolite shows superior performance over ion-exchange resins catalysts and possesses advantages due to its higher thermal stability and improved mass transfer. Researchers recently showed that heteropoly acid catalysts are suitable catalysts for the etherification reaction. This phenomenon conclusively proves that more research studies are needed to identify more promising catalysts for the etherification reaction and that new types of catalysts are expected to be revealed over time.

In general, the purification of ETBE involves complicated separation techniques because of the azeotropic mixtures that are formed between the reactants, products and by-products. Conventionally, a series of distillation columns and a washing column have been used for ETBE purification. Currently, easier separation routes have been discovered. Liquid–liquid extraction by ionic liquids and membrane pervaporation are recently discovered separation techniques. However, researchers are still attempting to develop a compact, environmentally friendly and energy- and cost-saving technique that results in the generation of higher-purity ETBE with minimum input. This result can be achieved only if the ETBE production and purification mechanisms are understood in depth. Simulation models are one of the approaches that are used to investigate, understand and evaluate the production and separation potentials of the new techniques. In this context, hybrid processes appear to be the most suitable design for the production of this compound. These hybrid processes are an energy- and cost-saving technique in which the heat released from the reaction can be used in the separation. In additional, the hybrid processes are favorable for equilibrium-limited reactions. Reactive distillation and pervaporation membrane reactors are good examples of hybrid processes.

Recently, nanomaterials, such as CNTs and graphenes, have been mainly used in the electronics field and not in chemical reactions. The buckypaper concept could be introduced for the fabrication of CNTs or graphenes into sheets or films that can be used in hybrid processes. These nanomaterials could serve as catalysts to facilitate the chemical reaction and as membrane materials for the pervaporation process. Functionalization is required to graft the desired $–SO_3H$ sulfonate group onto the surface of CNTs or graphene such that these groups can act as the catalyst active sites for the etherification reaction. Thus, the etherification reaction can occur on the surface of the catalytic membrane, and the undesirable component can be simultaneously removed from the reaction mixture via pervaporation. Thus, this hybrid process would promote the completion of the equilibrium-limited reaction. However, a key issue that needs to be addressed is the improvement of the strength of the buckypaper to achieve acceptable properties and characteristics. Moreover, there are some other limitations, including a reactor design to obtain good contact between the reactants and the catalytic membrane, as well as economical and commercialization aspects that need to be investigated. Therefore, experimental studies are required to facilitate and bring this new concept into a pilot-scale plant and ultimately large-scale commercialization.

Acknowledgements

The authors acknowledge USM fellowship supports from Universiti Sains Malaysia (USM). This research work was supported by a Membrane Cluster Grant and a Fundamental of Research Grant Scheme.

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